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Electronic Supplementary Information

Full-molar-ratio synthesis and enhanced lithium storage properties of Co_xFe_{1-x}CO₃

composite: an integrated lattice structure and an atomic-scale synergistic effect

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Table S1 Refined lattice parameters and unit-cell volumes of as-prepared $Co_xFe_{1-x}CO_3$ products (x = 0, 0.2, 0.4, 0.6, 0.8 and 1).

x in Formula $Co_x Fe_{1-}$	Latti	ce Parameters	Unit-Cell Volume		
_x CO ₃	a = b (Å)	<i>c</i> (Å)	v (Å ³)		
0	4.67990	15.34451	291.04		
0.2	4.67858	15.25931	289.26		
0.4	4.67065	15.18117	286.81		
0.6	4.66805	15.09220	284.81		
0.8	4.66343	14.96915	281.83		
1	4.66069	14.91493	280.58		



Fig. S1 The nearly linear relationship between the aspect ratio of composite $Co_xFe_{1-x}CO_3$ crystallites and the *x* value in the formula.



Fig. S2 Energy dispersive X-ray (EDX) analyses of serial $Co_xFe_{1-x}CO_3$ composites synthesized at the *x* value of (a) 0.2, (b) 0.4, (c) 0.6 and (d) 0.8.



Fig. S3 (a, b) Raman spectra of phase-pure CoCO₃ and FeCO₃ and serial xCoCO₃ + (1-x)FeCO₃ (x = 0.2, 0.4, 0.6 and 0.8) mixtures.

The low-wavenumber regions of these Raman spectra in panel (a) are magnified and shown in panel (b), highlighting that, as for mixture, its Raman characteristics can be visually assigned to those of phase-pure CoCO₃ or FeCO₃ crystallites.



Fig. S4 XRD patterns of time-dependent precipitates obtained from the reaction systems of (a) monocomponent $FeCO_3$, (b) monocomponent $CoCO_3$ and (c, d) composite $Co_{0.4}Fe_{0.6}CO_3$, and panel (d) highlights the integral structural characteristics of bicomponent composites.



Fig. S5 (left) SEM images and (right) XRD patterns of samples obtained in the absence of ascorbic acid (AA) for the hydrothermal syntheses of (a, b) two-component $Co_{0.4}Fe_{0.6}CO_3$, (c, d), mono-component FeCO₃ and (e, f) mono-component CoCO₃, respectively.



Fig. S6 (a) Comparative rate performances and (b) Nyquist plots of mono-component $CoCO_3$ and $FeCO_3$ electrodes, and an inset in panel (b) is the equivalent circuit of freshly assembled cells operated at open circuit voltages.

In the equivalent circuit, R_e , R_f and R_{ct} are the electrolyte resistance, the surface-film resistance of electrode and the charge transfer resistance, respectively, Q_1 and Q_2 represent the constant phase elements, and Z_w denotes the Warburg impedance.



Fig. S7 The 5th CV curves of CoCO₃, FeCO₃ and Co_{0.6}Fe_{0.4}CO₃ scanned at 0.2 mV s⁻¹ within the potential range of 0.01 and 3.0 V.

According to the peak positions and peak intensities of phase-pure $CoCO_3$ and $FeCO_3$ and also based on the *x* and (1-*x*) value in formula $Co_{0.6}Fe_{0.4}CO_3$, the 5th CV curve of $Co_{0.6}Fe_{0.4}CO_3$ could be regarded as the superimposition of those of phase-pure $FeCO_3$ and $CoCO_3$ (Fig. S7). In some sense, the enhanced electrochemical properties of the composite electrode can be attributed to an inner synergistic effect between Co- and Fe-based components within the structurally integrated crystallites of $Co_{0.6}Fe_{0.4}CO_3$.



Fig. S8 Comparative dQ/dV profiles of the 50th anodic-cathodic processes of $Co_xFe_{1-x}CO_3$ composites and corresponding $xCoCO_3 + (1-x)FeCO_3$ mixtures operated at 200 mA g⁻¹: (a), x = 0.2; (b), x = 0.4; (c), x = 0.6; (d), x = 0.8.

As shown above, the dQ/dV curve shape of each mixture electrode nearly depends upon the molar fraction (i.e., the *x* or (1-*x*) value) of dominant constitute (FeCO₃ or CoCO₃), which indicates there is almost no interactions between FeCO₃ and CoCO₃ in the mixture series.

Each composite electrode shows a novel dQ/dV curve different to that of FeCO₃ or CoCO₃, which could be regarded as a superimposition composed of the dQ/dV curves of FeCO₃ and CoCO₃. These suggest an inner interaction between Co-based and Fe-based components that exert a great influence on the enhanced electrochemical properties of the composite.



Fig. S9 (a, b) Comparative cycling stabilities of the four composite $Co_xFe_{1-x}CO_3$ and their corresponding mixture $xCoCO_3 + (1-x)FeCO_3$ electrodes operated at 200 mA g⁻¹, respectively. (c) Comparative retention rate of the 100th reversible capacities between composite $Co_xFe_{1-x}CO_3$ and mixture $xCoCO_3 + (1-x)FeCO_3$ electrodes at each *x* value, which is calculated according to their initial charge capacities operated at 200 mA g⁻¹ correspondingly.

Table S2 Capacity retention rates of composite $Co_xFe_{1-x}CO_3$ and mixture $xCoCO_3 + (1-x)FeCO_3$ electrodes (shown in Figure 6) calculated according to the 3rd discharge capacities operated at the activated current density of 100 mA g⁻¹.

	3rd Discharge	Capacity Retention Rate (%)				
Samples	(mAh g ⁻¹)	210th	220th	230th	240th	250th
Co _{0.2} Fe _{0.8} CO ₃	1164.9	87	88	89	90	91
0.2CoCO ₃ +0.8FeCO ₃	1110.3	93	89	87	86	84
Co _{0.4} Fe _{0.6} CO ₃	1265.9	95	96	97	97	99
0.4CoCO ₃ +0.6FeCO ₃	1084.1	86	82	81	77	76
Co _{0.6} Fe _{0.4} CO ₃	1185.7	94	98	98	98	99
0.6CoCO ₃ +0.4FeCO ₃	1134.8	85	82	79	77	77
Co _{0.8} Fe _{0.2} CO ₃	1358.1	90	90	91	92	93
0.8CoCO ₃ +0.2FeCO ₃	1219.5	86	85	83	82	83

Along with the continuous discharge-charge cycling, the capacity retention rate of each composite $Co_xFe_{1-x}CO_3$ electrode increase with the increasing cycle number, while that of each mixture $xCoCO_3$ + (1-*x*)FeCO₃ electrode decreases with the increasing cycle number.

When the *x* value in formula $Co_xFe_{1-x}CO_3$ is close to 0.5 (i.e. x = 0.4 or 0.6), the corresponding composites express a higher capacity retention rate in each cycle than the other two composites, suggesting a more homogeneous distribution of Co- and Fe-based components with a stronger inner synergistic effect.

Samples	$R_{e}\left(\Omega ight)$	$Q_{1}\left(\Omega\right)$	$R_{f}(\Omega)$	$\mathrm{Q}_{2}\left(\Omega ight)$	$R_{ct}(\Omega)$	$Z_{w}\left(\Omega ight)$
FeCO ₃	5.424	9.176×10-6	1.476×10^{16}	3.214×10-4	635.2	1.171×10-3
0.2CoCO ₃ + 0.8FeCO ₃	3.618	1.158×10 ⁻⁵	2.610×10^{7}	6.845×10 ⁻⁴	611.7	1.687×10 ⁻³
$Co_{0.2}Fe_{0.8}CO_3$	2.387	8.687×10 ⁻⁶	8.238×10^{18}	7.068×10 ⁻⁴	582.0	1.211×10 ⁻³
0.4CoCO ₃ + 0.6FeCO ₃	3.869	8.606×10-6	1.112×10^{13}	7.617×10-4	547.1	1.509×10-3
$Co_{0.4}Fe_{0.6}CO_3$	3.777	1.608×10 ⁻⁵	1.130×10^{18}	5.113×10 ⁻⁴	536.9	1.186×10 ⁻³
0.6CoCO ₃ + 0.4FeCO ₃	3.359	8.288×10 ⁻⁶	5.068×10^{7}	6.432×10 ⁻⁴	472.2	1.451×10 ⁻³
$Co_{0.6}Fe_{0.4}CO_3$	4.366	9.371×10 ⁻⁶	1.100×10^{14}	6.387×10 ⁻⁴	453.3	1.301×10 ⁻³
0.8CoCO ₃ + 0.2FeCO ₃	4.306	1.275×10 ⁻⁵	2.892×10^{9}	7.244×10 ⁻⁴	455.2	1.607×10 ⁻³
$Co_{0.8}Fe_{0.2}CO_3$	5.394	1.381×10-5	1.746×10^{16}	5.524×10-4	416.5	1.903×10 ⁻³
CoCO ₃	4.047	1.958×10 ⁻⁵	9.745×10 ⁹	1.247×10 ⁻⁴	374.6	1.491×10 ⁻³

Table S3 EIS parameters of full-molar-ratio composite $Co_xFe_{1-x}CO_3$ ($0 \le x \le 1$) and the corresponding mixture $xCoCO_3 + (1-x)FeCO_3$ derived from an equivalent circuit.

Based on an equivalent circuit, the fitted R_{ct} values of both composite $Co_xFe_{1-x}CO_3$ and mixture x $CoCO_3 + (1-x)$ FeCO₃ decrease with the increase of component CoCO₃ content (i.e., x value), which are similar to the values of 635.2x + 374.6(1-x) calculated according to the R_{ct} values of phase-pure FeCO₃ (635.2 Ω) and CoCO₃ (374.6 Ω).

By comparison, at each *x* value, the obtained R_{ct} value of composite $Co_xFe_{1-x}CO_3$ is lower than that of the corresponding mixture $xCoCO_3 + (1-x)FeCO_3$.



Fig. S10 (a) Representative N_2 adsorption-desorption isotherms and (b) pore size distributions of $Co_{0.6}Fe_{0.4}CO_3$ composite and corresponding $0.6CoCO_3 + 0.4FeCO_3$ mixture.

Both of the N₂ adsorption-desorption isotherms can be approximately classified as type IV isotherms with a type H3 hysteresis loop, and the specific surface areas (i.e., the Brunauer-Emmett-Teller, BET, surface areas) are 4.01 and 2.56 m² g⁻¹ for the $Co_{0.6}Fe_{0.4}CO_3$ composite and corresponding 0.6CoCO₃ + 0.4FeCO₃ mixture, respectively. The relatively small BET areas as well as the less prominent pore size distributions indicate that both of them are lack of porous natures.